QUALITY MONITORING AND SAFETY

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INVERSION VOLTAMMETRY FOR DETERMINING CONTENT OF CHROMIUM RELEASED FROM HOUSEWARE

A. M. Braikova,[1] N. I. Zayats,[1] and N. P. Matveiko[1]

A method for inversion voltammetric determination of the content of chromium released into model media from houseware is developed. The optimum conditions for analyzing chromium content are established: the background electrolyte — HNO_3 of concentration 0.4 M, accumulation of chromate ions on the surface of C/Ag electrode under potential of $+ 200$ mV for $60 – 80$ sec, registration of the voltammetric curve from $+ 200$ to $– 350$ mV at the potential sweep rate of 600 mV/sec.

Houseware, including glass, glass ceramic, ceramic, and enamel ware used for preparing and storing food products should not impair the quality of food or release agents dangerous to human health into food. The parameters of toxic emissions are safety parameters that characterize the sanitary-hygienic properties of a surface and its resistance to the effect of acid media contained in food products.

Sources of dangerous compounds can be glass, glass ceramics, ceramic glazes, and enamels which under the effect of food can release toxic elements, such as lead, cadmium, aluminum, as well as microelements: zinc, barium, chromium, boron, cobalt, copper, etc. For microelements to be dangerous, its dose must be rather high; however, they are able accumulate in a living organism. Therefore, even small quantities of them may cause negative consequences over time.

Although the quantities of toxic agents released from houseware may seem insignificant, they should be analyzed in the contex of the general impact of toxic elements on humans, which keeps increasing with technical progress. Therefore, the content of toxic agents released from household food containers is regulated by international and national standards (ISO 7086–82, ISO-8391–86, GOST 25185–98), etc.

The Russian Federation and the Republic of Belarus have standards established by the health system (GN 2.3.3.972–00 and SanPiN 13-3 2001), which require the quantities of toxic agents released from houseware not to exceed the prescribed admissible migration concentration (AMC). The AMC is the main criterion for evaluating products during their development, production, and certification. Furthermore, some chemical elements, such as boron, zinc, titanium, aluminum, lead, barium, cadmium, and chromium, should be periodically monitored in industrial products.

The migration level of chemical substances is determined in model media (distilled water, weak acid solutions, etc.) simulating the properties of an expected food product range under temperature-time conditions reproducing real service conditions.

One of the elements whose migration level is regulated by the current sanitary norms is chromium. Its effect on a human organism is classified as class 3 danger: a moderately dangerous agent (GOST 12.1009–76). The International Agency for Cancer Research classifies chromium as a carcinogenic agent; being biologically mobile, it damages mucous membranes, skin, kidney, and other organs.

Chromium is an effective ionic colorant (intense coloring emerges already with 0.1% Cr_2O_3 content) that may exist in glass and vitreous coatings in two degrees of oxidation, namely Cr^{3+} and Cr^{6+}, whose weight ratio determines the degree of color intensity. Chromium compounds that are most frequently used as colorants are potassium dichromate combined with oxides as cooper, iron, or less frequently cobalt. Depending on glass composition and melting conditions, chromium compounds tint glasses green, yellow-green, or yellow.

It is established by the sanitary norms that the total content of chromium (Cr^{3+}, Cr^{6+}) released into specially prepared model media should not exceed 0.1 mg/liter. The

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[1] Belarus State Technological University, Minsk, Belarus.

quantity of chromium released from houseware depends on the chemical resistance (mainly acid resistance) of glasses, enamels, and ceramic glazes, which, in turn, depends on many structural, technological, and other factors.

The problem of increasing acid resistance and, consequently, decreasing the release of toxic materials is topical and has to be solved integrally by optimizing the composition of glasses, vitreous coatings, glazes, and enamels, as well as improving technology and intensifying quality control.

Efficient control methods and instruments are needed to monitor the safety parameters of the products. These methods should be highly sensitive (as the quantity of released toxic agents is insignificant), selective (theoretically any element contained in glass may be present in the solutions), simple, and fast.

There are two standard methods for determining the content of chromium in model media, i.e., atomic absorption and photocolorimetric methods (GOST 24295–80). Other promising methods are based on electrochemical reactions, in particular, the inversion voltammetry method. It finds wide application in determining small quantities of metals in various ambient objects as it is easy to use, fast, and does not require expensive equipment or reactants.

The inversion voltammetry method is based on electrochemical (cathode or anode) accumulation of a desired metal on a revolving solid electrode with its subsequent dissolution. In doing so, a voltamperogram (the dependence of current I on the metal dissolution potential) is registered, where the positions of the current peaks on the potential axis qualitatively identify the metals analyzed (each metal corresponds to a particular dissolution potential) and the height of the peak is proportional to the concentration of this metal in the solution.

The literature describes several methods for inversion-voltammetric determination of chromium content using various background electrolytes, indicator electrodes, and methods of chromium accumulation on the surface of the indicator electrode. However, most of them require expensive reactants and rigid conditions of analysis.

The purpose of the present study was the development of a procedure for determining the content of chromium in aqueous solutions by inversion voltammetry.

Experiments were carried out on an AVA-2 voltammetric analyzer couple with an IBM PC in a three-electrode cell. The indicator electrode was a modified carbon-pyroceram rod with a working surface area of 0.13 cm^2. The reference electrode was a saturated silver chloride half-cell and the auxiliary one was made of platinum wire.

It is known that one of the methods for concentrating metals involves oxidation or reduction of their variable-valence ions and formation of a poorly soluble compound on the surface of the indicator electrode [1–4].

We have investigated the possibilities of using such compounds as Hg_2CrO_4, Ag_2CrO_4, and $CuCrO_2$ for chromium concentration. The anode oxidation of the copper, silver, and mercury electrodes produces copper, silver, and mercury ions

which in the presence of chromate ions are accumulated on the surface of the indicator electrode in the form of poorly soluble salts and do not have time to diffuse in the depth of the solution. As a result, Hg_2CrO_4, Ag_2CrO_4, or $CuCrO_4$ is accumulated on the surface of the indicator electrode and their quantity depends on the concentration of chromate ions. The subsequent registration of a cathode voltammetric curve of metal ions reduced from poorly soluble compounds makes it possible to determine the concentration of chromate ions in the solution. The maximum current of metal reduction is the analytic signal for determining the chromate ions.

Optimum results were obtained using a carbon-pyroceramic rod modified with silver (C/Ag electrode). A silver film on the surface of the carbon-pyroceramic electrode was accumulated from an aqueous electrolyte solution containing 0.1 M HNO_3 and 0.1 M Ag_2NO_3. Silver was electrochemically precipitated for 250 sec at a temperature of 298 K and a potential of -600 mV. Before precipitation the indicator electrode was anodically polarized under a potential of $+500$ mV in 1.0 M HNO_3 solution for 5 min to cleanse its surface. The duration and the accumulation potential were determined experimentally to satisfy the requirements on continuity and density of the silver film on the carbon-pyroceramic carrier.

The inversion-voltammetric determination of chromium content requires optimization of the following measurement conditions: the composition and concentration of the background electrolyte, as well as the potential and duration of chromium accumulation in the form of poorly soluble chromate on the surface of C/Ag electrode.

To select an optimum background electrolyte ensuring electric conductivity in the electrochemical cell, we carried out experiments using aqueous solutions of HNO_3 and H_2SO_4 of concentration $0.1–0.8$ M, since silver nitrates and sulfates are soluble salts. It has been established that when the background electrolytes have concentrations of $0.5–0.8$ and $0.1–0.2$ M, the range of recognizable chromium concentrations becomes narrower and the relative error grows (to $30–40\%$). A clearly expressed current maximum of silver chromate reduction is registered in the solution of background electrolytes HNO_3 or H_2SO_4 of concentration 0.4 M; consequently, these background electrolytes have been selected as optimal ones.

In determining the optimum potential of chromium accumulation in the form of a poorly soluble chromate in 0.4 M HNO_3 solution using a carbon-pyroceramic electrode modified by silver, cathode voltammetric curves were registered for different concentrations of chromium ions under accumulation potentials of $+150$, $+190$, $+200$, $+230$, and $+250$ mV. The content of chromium in the cell was 2×10^{-8} M, and the accumulation lasted 60 sec. The regeneration of the electrode proceeded under the potential of -300 mV for 20 sec. The obtained results are shown in Fig. 1.

The voltammetric curves registered under accumulation potentials of $+230$ and $+250$ mV have significant distor-
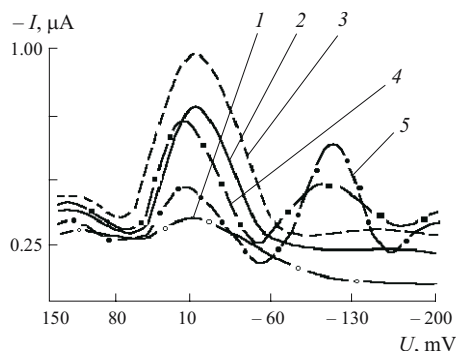
Fig. 1. Averaged voltammetric curves of carbon-pyroceramic electrode modified by silver (chromium concentration in solution 2×10^{-8} M, sweep rate 600 mV/sec). Potential of silver chromate accumulation: *1, 2, 3, 4,* and *5*) 150, 190, 200, 230, and 250 mV, respectively.
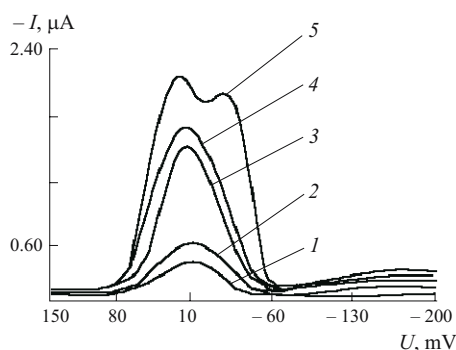
Fig. 2. Averaged voltammetric curves of carbon-pyroceramic electrode modified by silver (chromium concentration in solution 2×10^{-7} M). Duration of silver chromate accumulation: *1, 2, 3, 4,* and *5*) 20, 40, 60, 80, and 100 sec, respectively.

tions, which impedes the quantitative determination of the chromium content. The current maximum on the voltammetric curve registered after the accumulation of material under the potential of $+150$ mV is insignificant, which shows the difficulty of accumulating silver chromate under such potential and, consequently, the impossibility of the quantitative determination of chromium content.

With accumulation potentials $+190$ and $+200$ mV the cathode voltammetric curve has no distortions and there is a clearly defined maximum of current caused by the reduction of silver chromate concentrated on the indicator electrode. The optimum potential of chromium accumulation in the form of silver chromate is $+200$ mV, since in this case the limiting diffusion reduction current is slightly higher than under the potential of $+190$ mV.

It is known that accumulation duration depends on the concentration of the component analyzed in the solution. As its concentration grows, the accumulation duration decreases. However, for each analyzed metal it is necessary to identify its optimum accumulation duration. For this optimization we have registered cathode voltammetric curves for

accumulation of silver chromate lasting 20, 40, 60, 80, and 100 sec. The concentration of chromium in the solution was 1×10^{-7} M. Figure 2 shows the comparative results of this study.

It can be seen that the optimum accumulation duration is $60 - 80$ sec, as these voltammetric curves have a single clearly defined maximum of silver chromate reduction current, which makes it possible to determine chromium content in the solution with a relative error of not more than 5%. A decrease in accumulation duration significantly decreases the strength of the limiting diffuse current; accordingly, the method sensitivity decreases and the relative error grows $(10 - 20\%)$. As the accumulation duration increases (100 sec and more), we observe distortions on the voltammetric curves, presumably caused by perceptible destruction of the silver film under a protracted effect of the anode current, which impedes the determination of chromium content in the solution and increases the relative error up to 30. A similar effect of accumulation duration on the error and the method sensitivity is observed under other concentrations of chromium in the solution.

Thus, the following optimum conditions have been established: for determining chromium content: background electrolyte — aqueous solution of HNO_3 of concentration 0.4 M, accumulation of chromate ions on the surface of C/Ag electrode under a potential of $+200$ mV for $60 - 80$ sec, registration of the voltammetric curve from $+200$ mV to -350 mV at the potential sweep rate of 600 mV/sec.

The developed method was used to determine the content of chromium released from houseware into model media: distilled water, 10% alcohol solution, and 4% acetic acid solution. The model media were poured into glass, enamel, and glazed ceramic chromium-tinted ware and held away from light at $20 \pm 5°C$ for 24 h ± 10 min.

Chromium in model media (samples) exists mainly in the trivalent state. Therefore, we performed additional preparation of the sample when Cr^{3+} was oxidized to Cr^{6+}. For this purpose, a 100 ml sample was boiled for $25 - 30$ min, and ammonium sulfate was added to obtain a moist precipitate. After oxidizing, each sample was dissolved in 20 ml of the background electrolyte (0.4 M solution of HNO_3). Next, all obtained solutions were analyzed and the unknown concentration was determined by the additive method. The arithmetic mean of three measurements was taken as the result.

We have calculated the metrological characteristics of the developed method for determining the content of chromium according to MI 2336. The calculation shows that the relative total error in the range of chromium concentrations of $0.01 - 0.50$ mg/dm^3 does not exceed 22%. The operational reproducibility control norm is 15% and the recurrence norm is 14%.

The proposed method can be used to determine the content of chromium released from houseware into model me-

dia. This method has been certified by the State Standard Committee of the Republic of Belarus.

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